

**Input-Output Budgets of Major Ions, Trace
Elements and Mercury for a Forested Watershed
in Western Maryland**

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ABSTRACT

This field study, sponsored by the Maryland Power Plant Research Program, was conducted to increase our understanding of the retention and movement of major ions and trace elements in forested watersheds. Atmospheric inputs (precipitation and throughfall) and stream water export of major ions, trace metals, and mercury from a completely forested watershed in western Maryland were measured from June 1996 through May 1997. Results were used to estimate major ion, trace metal, and mercury export; examine regional patterns in wet deposition and canopy-atmosphere interactions; and compute input-output budgets for HCWS.

Results indicate that HCWS: receives some of the highest atmospheric inputs of H^+ , NH_4^+ , NO_3^- and SO_4^{2-} in the eastern U.S.; is a net sink for H^+ , NH_4^+ , NO_3^- and K^+ ; and is exhibiting signs of N saturation. A strong regional gradient in wet deposition of many trace elements was observed (e.g., wet deposition was highest in western Maryland, intermediate in central Maryland, and lowest near the East Coast). This pattern reflects both closer proximity to regional sources and higher precipitation rates in the Allegheny Plateau.

The forest canopy has little effect on the deposition of Al, As, and Pb; however, the canopy was a net source of Mn, Fe, Cu, Zn, and Se. Input-output budgets suggest that atmospheric inputs of Al equaled stream water outputs; 50-90% of the atmospheric inputs of Pb, As, and Se were retained in HCWS; 25% of the atmospheric inputs of Fe, Cu and Cr were retained; and HCWS is a net source of Zn, Ni and Cd.

Wet deposition flux of Hg to western Maryland is similar to that of other rural sites in Maryland; variability between sites and years is largely a function of differences in rainfall amounts. The concentration of total Hg in precipitation did not correlate strongly with any other major ions or trace elements, suggesting that no particular source profile predominates. Comparable to other forested watersheds, the yield of Hg from the stream is low, suggesting a buildup of Hg in soils.

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EXECUTIVE SUMMARY

The Maryland Power Plant Research Program (PPRP) sponsored this study, the Western Maryland Atmospheric Deposition Study, to extend the spatial coverage of wet deposition data to the western portion of the Chesapeake Bay watershed. The three primary goals of this project were to:

- Determine spatial variability in major ions and metals deposition across the watershed, using existing data for the Piedmont Region and Coastal Plain available from the literature, and new data collected during the field portion of the current study;
- Estimate total wet deposition of major ions and selected trace elements to the Bay and its tributary regions using data sets developed for each region; and
- Determine the relationship between precipitation inputs to a forested watershed in western Maryland and annual stream water export of these same trace elements.

The project was a cooperative effort sponsored by PPRP and conducted by researchers from the University of Maryland Center for Environmental Science Appalachian Laboratory (AL) and Chesapeake Biological Laboratory (CBL); and from the University of Delaware College of Marine Studies (UDEL).

The goal of this portion of the study as reported here was to increase our understanding of the retention and movement of major ions and trace elements in forested watersheds. To accomplish our goal, we measured atmospheric inputs (precipitation and throughfall) and stream water export of major ions, trace metals and mercury from a completely forested watershed in western Maryland from June 1996 through May 1997. Precipitation was measured on a daily basis at the Piney Dam in Garrett County, Maryland. Throughfall and stream water chemistry were measured on a weekly basis at an unnamed tributary to Herrington Creek in the Herrington Creek Watershed (HCWS). Continuous stream water discharge from HCWS was used with our stream chemistry data to estimate major ion, trace metal and mercury export from HCWS. These data were used to examine regional patterns in wet deposition, canopy-atmosphere interactions, and to compute input-output budgets for HCWS.

Wet deposition was an important source of major ions, trace elements and mercury. Among the major ions, H^+ ($728 \text{ eq ha}^{-1} \text{ yr}^{-1}$), SO_4^{2-} ($562 \text{ eq ha}^{-1} \text{ yr}^{-1}$), NO_3^- ($312 \text{ eq ha}^{-1} \text{ yr}^{-1}$), and NH_4^+ ($170 \text{ eq ha}^{-1} \text{ yr}^{-1}$) had the highest annual wet deposition rates, which are similar to those reported for other high deposition sites in the northeastern United States. For the trace metals, Al, Fe and Zn had the highest wet deposition rates ($3000\text{--}11000 \mu\text{g m}^{-2} \text{ yr}^{-1}$); Cr, Cu, Mn, Ni, Pb and Se had intermediate rates ($200\text{--}800 \mu\text{g m}^{-2} \text{ yr}^{-1}$); and Cd and As had the lowest rates ($\sim 100 \mu\text{g m}^{-2} \text{ yr}^{-1}$). Annual wet deposition of total mercury was $14.9 \mu\text{g m}^{-2} \text{ yr}^{-1}$ and wet deposition of methylmercury was less than 1% of the total mercury deposition.

The forest canopy had a major effect on most major ions (K^+ , Ca^{+2} , Mg^{+2} , SO_4^{2-} , and NO_3^-) and one trace metal (Mn); some effect on a few trace elements (Fe, Ni, Zn, Cd, Cr, Cu, Se); and little to no effect on a few major ions (Na^+ and NH_4^+), trace elements (Al, As and Pb) and total mercury. On an annual basis, the forest canopy consumed 20% of the free acidity in incident precipitation, had no net effect on Na^+ and NH_4^+ deposition, and was a strong net source of K^+ , Ca^{+2} , Mg^{+2} , SO_4^{2-} , NO_3^- and Mn. The enhanced (1.5 to 60 times greater than wet deposition) throughfall of these ions was due to canopy exchange reactions and leaching of dry deposited gases and particles. For trace metals, the canopy was a small net source of Fe, Cu, Zn, and Se; throughfall deposition rates were 30 to 50% greater than wet deposition, and were consistent with expected dry deposition rates. In contrast, the canopy was a net sink for Ni, Cd, and Cr. For mercury, annual throughfall deposition rates for total mercury were about 30% greater than wet deposition rates. We assume this is due to the wash-off of dry deposited material.

On an annual basis, HCWS retained essentially all of the throughfall inputs of H^+ and NH_4^+ , about 35% of the throughfall inputs of K^+ and NO_3^- , and was a net source of SO_4^{+2} , Cl^- , Ca^{+2} , Mg^{+2} , and Na^+ . Export of these ions was 2 to 5 times greater than the throughfall inputs. For the trace metals, atmospheric inputs equal stream water outputs of Al and Mn, inputs are 2 to 3 times lower than outputs for Zn, Ni, and Cd, and the watershed is a net sink for Fe, As, Cu, Pb, Se, and Cr. From among the elements (Fe, As, Cu, Pb, Se and Cr), Pb, As and Se are most strongly retained in the HCWS, representing a 50 to 90% retention of the atmospheric input. For Fe and Cu and Cr, only about 25 % of the atmospheric input is retained by HCWS. For mercury, about 80% of the atmospheric input was retained by the watershed.